Degradation Kinetics of Isoproturon and its Subsequent Products in Contact with TiO_2 Functionalized Silica Nanofibers

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Abstract:

A challenge for the photodegradation of (organic) micro-pollutants in waste water treatment is the mechanistic and kinetic understanding beyond the degradation of the initial (parent) harmful product, e.g. the phenylurea herbicide isoproturon (IPU). By combining liquid chromatography – mass spectrometry and kinetic Monte Carlo modeling, we demonstrate that upon optimizing the dip-coating conditions (0.34 mol L^{-1} TiO_2 solution at a coating speed of 160 mm min^{-1}) for the functionalization of a superhydrophilic electrospun silica nanofibrous membrane (i) hydroxylation is a dominant reaction pathway and (ii) once IPU reacts on the surface of the TiO_2 nanoparticles, further hydroxylation occurs sufficiently fast, with complete IPU removal under the detection limit (5-10 mg $L_{solution}^{-1}$) as a result of UV irradiation within 8 hours. As hydroxylation is dominant, degradation intermediates with a higher water solubility are formed and therefore a decreased toxicity is obtained upon reintroducing the treated solution into the environment. This is confirmed by respirometry, with an increase in the oxygen uptake rate of an activated sludge from 5.9 mg O_2 $g_{activated\ sludge}^{-1}$ h^{-1} for an untreated 10 mg L^{-1} IPU solution to 8.2 mg O_2 $g_{activated\ sludge}^{-1}h^{-1}$ for a solution irradiated for 8 hours, in line with a blank solution.

Keywords: Photodegradation kinetics, Water treatment, Electrospinning, Kinetic Monte Carlo modeling, Respirometry, Hydroxylation

1. Introduction

Waste water treatment is an important (bio)chemical engineering activity due to the increasing shortage in clean water and the demand for better reusability [1–3]. Advanced oxidation processes (AOPs) are a key for such treatment and therefore new AOP techniques are being developed and employed to degrade pollutants in waste streams *via* chemical oxidants with or without the assistance of radiation [4,5]. Lacking is the limited mechanistic and kinetic understanding, not only covering the disappearance rate of the harmful parent component, but also the subsequent (net) rates defining the overall mineralization process in several generations of degradation product types [6–10]. Only in that way, one can evaluate the true time at which less harmful products are dominantly present and thus acceptable treatment has been achieved.

Specific focus has been placed on the degradation of phenylurea herbicides, e.g. isoproturon (IPU), that are widely used for the growth control of most broad-leaved weeds and annual grasses, although they are toxic and generate hazardous chemicals contaminating water streams [11–14]. IPU has unfortunately a relatively high solubility in water and low (bio)chemical degradation rates (time to 25% dissipation between 1 to 13 weeks [15–17]) and is therefore easily leached in water bodies [18]. In addition, it has a strong tendency towards bioaccumulation or biomagnification, causing health issues such as poisoning, cancer, neurological effects and reproductive and developmental effects [12,19,20].

The non-biodegradability of IPU combined with the knowledge that it cannot be completely removed by conventional methods such as treatment with activated carbon opened up the world of AOP research for waste water purification [4,8,11,12]. Especially the use of heterogeneous catalysts in AOPs, e.g. in photocatalysis, are under intensive research for their simplicity and reusability [6–8,21]. Heterogeneous photocatalysis based on a porous substrate with the

incorporation of titanium dioxide (TiO_2) particles is currently considered as a promising technique for the degradation of herbicides, as illustrated at the bottom of **Fig 1** [4,5,22–27]. As semiconductor, TiO_2 induces a series of reduction and oxidation reactions on/close to its surface upon irradiation with light equal to or greater than the semiconductor's band gap (e.g. 3.10 eV for rutile and 3.23 eV for anatase) [28–32]. The modified oxygen species and the photogenerated "electron-hole pair" participate in the degradation of organic pollutants, resulting in the mineralization of the herbicide in several generations, **Fig 1f** [20,33,34].

A natural question that arises is the identification of the most suitable porous substrate. In this respect, nanofibrous membranes, produced via electrospinning, have a high specific surface area, high porosity, small pore size, and allow a high liquid flux, which makes these membranes ideal candidates for the immobilization of photocatalytic active TiO_2 particles [26,36–42]. The electrospinning process allows for production of both polymeric and ceramic nanofibrous membranes [37], with ceramic nanofibers having the advantage of a superior thermal and chemical resistance which allows for their use in highly acidic industrial effluents [43–46]. Moreover, they are much less susceptible to the deterioration of hydroxyl radicals, enabling long-time use in AOPs [47].

Recently, we successfully produced ceramic silica nanofibers without the need of a sacrificial polymer, **Fig 1a-c** [35,48,49]. In contrast to other work, in which a well-spinnable organic polymer is mixed with a metal oxide precursor to facilitate the electrospinning process, direct electrospinning of a tetraethyl orthosilicate (TEOS) precursor eliminates the need for a post-production removal of the organic polymer [37,50,51]. This results in dense silica nanofibers with superior mechanical properties, allowing use in water and effluent remediation [35,43,51]. After electrospinning the membrane is highly hydrophobic with a water contact angle (CA)

larger than 140°. A wettability switch to a superhydrophilic membrane (water CA < 5°) is obtained by applying a thermal treatment (e.g. 500°C; hour scale), with in addition a further increase of the silica network density **Fig 1d** [35,52,53]. Functionalization of these nanofibers with TiO_2 nanoparticles results in an added value for removal/degradation of organic components, **Fig 1e**. In addition, this functionalization prevents fouling of the membrane, a major issue in membrane applications [54–56]. Previous research already showed that functionalization with TiO_2 nanoparticles by dip-coating, enables a very high degradation rate of IPU [57]. This avoids suppression of the photocatalytic activity by UV-shielding with an inert silica layer onto the TiO_2 nanoparticles when compared to the incorporation of TiO_2 nanoparticles in the sol-gel before nanofiber synthesis [58,59].

The photocatalytic degradation of various organic compounds, such as IPU, over TiO_2 is often assumed to follow pseudo first-order reaction kinetics (formally on a mass basis):

$$\ln\left(\frac{c}{c_0}\right) = -kt \tag{1}$$

with c the mass concentration of the starting organic compound after UV irradiation at time t, c_0 the initial mass concentration, and k the "degradation rate coefficient" in s^{-1} [57,60–66]. Product spectra for the formed subsequent degradation products have been additionally suggested but without a real focus on the time dependencies of the concentrations of the complete degradation process [67–71]. The monitoring of the reactive species during the photocatalytic effluent treatment, their degradation pathways and byproducts analysis play although a key role in order to determine the process efficiency and to evaluate the best method in terms of further treatment by biological processes [6,72,73].

A more intensive investigation of the photocatalytic mineralization is therefore still recommended, and the present work aims at closing the gap by kinetically investigating the

photocatalytic degradation of IPU using immobilized TiO_2 nanoparticles onto a silica nanofibrous substrate. Focus is placed on the functionalization characteristics, the degradation pathway and the overall kinetics for several generations of degradation products, as conceptually highlighted at the bottom of **Fig 1**. The recorded liquid chromatography – mass spectrometry (LC-MS) experimental data are interpreted based on kinetic Monte Carlo (*k*MC) simulations [73] to better understand the connection of several generations of degradation products/intermediates [74,75]. It is further demonstrated that the degradation kinetics cannot be grasped by applying kinetic modeling studies for which the quasi-steady-state approximation (QSSA) is applied for the calculation of the concentrations of the reactive intermediates. In addition, combined with respirometry experiments, a genuine time scale for the mineralization process to achieve sufficiently harmless substances is reported for the first time.

2. Materials and experimental methods

2.1. Materials

For the electrospinning process, the sol-gel precursor tetraethyl orthosilicate (TEOS, reagent grade 98%) and the catalyst (hydrogen chloride; HCl, 37%) were obtained from Sigma-Aldrich and used as received. The solvent, ethanol absolute, was obtained from Fiers. Titanium (IV) oxide, Degussa P 25, was obtained from Sigma-Aldrich. It is a standard material in the field of photocatalytic reactions, with an average particle size of *ca.* 20 nm and a specific surface area of 35-65 $m^2\ g^{-1}$. To test the degradation of isoproturon (IPU), PESTANAL analytical standard was obtained from Sigma-Aldrich.

2.2. Electrospinning of TEOS-based nanofibers for membrane production

Silica nanofibers were made using the methodology described in previous work [35,48,49]. A solution of TEOS, ethanol, distilled water and HCl at initial molar ratios of 1:2:2:0.01 was used. The TEOS is first mixed with ethanol, and in a second stage the aqueous HCl solution is added under vigorous stirring. After the exothermic hydrolysis step (5 to 10 minutes), the solution is heated up to 80°C under stirring until a viscosity between 120 and 200 mPa s is reached. Prior to electrospinning the viscosity of the solutions was measured using a Brookfield viscometer LVDV-II. The electrospinning experiments were executed on a rotating drum collector using a dual moving needle set-up. The tip-to-collector distance was fixed at 15 cm, the flow rate at 1 mL h^{-1} and the voltage was adjusted between 20 and 22 kV to obtain a stable electrospinning process. All the experiments were executed at 21°C ± 2°C. Nanofibrous membranes with a density of approximately 10 g m^{-2} were obtained.

Note that purchase of an industrial electrospinning equipment is comparable to the cost price of a typical textile coating line. Since it is possible to have a continuous production of electrospun nanofibrous membranes, a direct dip-coating could can be incorporated in the production line without a large increase in cost price. The largest cost of the total process will be the provision and energy consumption of the UV-sources, which is in line with other photocatalysis applications.

2.3. Functionalization and characterization of the electrospun silica nanofibers

Aqueous TiO_2 nanoparticles suspensions (molar concentrations of 0.05 mol L^{-1}, 0.34 mol L^{-1}, and 0.50 mol L^{-1}) were dip-coated on the membranes at room temperature at various coating speeds (80 and 160 mm min^{-1}) in a clean room facility (class 100,000/1000). A computer controlled dip-coating unit (KSV Instruments) was used. The samples were immersed for 3 min, dried at room temperature for 24 hours, washed with distilled water, and dried at room temperature. As a result the TiO_2 particles are sufficiently fixated on the membranes.

The morphology and the diameters of the nanofibers were examined using a FEI Quanta 200 F Scanning Electron Microscope (SEM) at an accelerating voltage of 20 kV. Prior to analysis the samples were coated using a sputter coater (Emitech SC7620, Au coating). Image J software was used to determine the nanofiber diameters by taking an average of 50 measurements. The water contact angle was determined using a DSA 30 Krüss GmbH drop shape analyzer. A demineralized water droplet of 2 µL was placed on the membrane surface, after which the contact angle was obtained by curve fitting of the stable droplet. The TiO_2 loading was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis and X-ray Diffraction (XRD) analysis (details see Supporting Information). The clean water permeability (CWP) before and after functionalization were determined using a flow through system as described in Bjorge et al. [76] and Daels et al. [77] by measuring the flux at different trans-membrane pressures.

2.4. Photocatalytic activity experiments for the functionalized membranes

Evaluation of the photocatalytic activity of the membranes was performed by analyzing the photodegradation of an aqueous IPU solution (initial mass concentrations ($c_{IPU,0}$) of 5 and 10 mg L^{-1}) under UV irradiation. The set-up is given in **Fig S1** in the Supporting Information. Three samples have been tested simultaneously and between three and nine samples were tested for each type of membrane. The data shown are the average of these measurements. The samples were fixed in a circular sample holder with a diameter of 4.5 cm (resulting in a membrane with a mass of approximately 16 10^{-3} g) and immersed in a tempering beaker (at 15°C) containing 100 mL of the IPU solution and illuminated from a distance of 13 cm by a 300 W Osram Ultra-Vitalux lamp. The lamp emits radiation with an average intensity of about 5 mW cm^{-2}, mainly ultraviolet light. The lamp was switched on 1 hour before starting the photocatalytic test to stabilize the power of the emission spectrum. To ensure the attainment of the adsorption equilibrium the samples were immersed in the solutions 24 hours prior to the photocatalytic test. Note that for illustration purposes focus is on conventional conditions and not harsh conditions as the suitability of silica-based systems is well-established. Furthermore, for scale-up a maximal membrane size can be defined, which implies in practice sufficient interconnected contact times.

The IPU degradation was followed by measuring the transmission spectra of the solutions on a regular basis using (i) a Perkin-Elmer Lambda 900 UV-Vis spectrophotometer and (ii) Liquid Chromatography – Mass Spectrometry (LC-MS). The former equipment is used to assess the relative signals of all photoactive compounds and the latter to study the connectivity of degradation products.

Sampling was done after 1, 2, 3, 4, 6, 8, 10, 12, and 24 hours of illumination, after which the concentration of all UV active compounds was measured by recording the absorbance at 241 nm with a UV-Vis spectrophotometer. The percentage of degradation was expressed as $100 \times (c_0-c_x)/c_0$, with c_0 the mass concentration of IPU before the experiment (5 mg L^{-1}) and c_x the concentration of all photoactive compounds at a certain time.

The LC-MS system consists of a Surveyor HPLC coupled to a Quantum Discovery mass spectrometer (Thermo Scientific) equipped with an electrospraying source, operated in full scan positive ionization mode for the detection of the IPU. For the detection of the degradation compounds, tandem mass spectrometry was applied. The mass spectrometric parameters for the degradation compounds are presented in **Table 1**.

Table 1. Mass spectrometric parameters for the degradation compounds.

Compound	PI (*m/z*)	CE (eV)	FI (*m/z*)
B_1	223	20	165
B_2	223	20	181
B_3	223	20	178
C_1	239	20	150
C_2	239	20	165
D_1	255	20	72
D_2	255	20	72
Betamethasone	393	35	147

PI: precursor ion; CE: collision energy; FI: fragment ion

The samples were diluted twice with a methanolic solution to ensure measurement in the linear dynamic range of the mass spectrometer without causing interference, containing an internal standard (betamethasone, 1 µg mL^{-1}) prior to analysis. Afterwards, 1 µL (starting value) was injected. The separation was performed on a Omnispher C18 column 50 x 3 mm (3 µm particle size) protected with a guard column 10 x 2 mm (both from Varian). The mobile phase consisted of water and methanol, both containing 0.1% acetic acid (volume basis) and 1 mmol L^{-1}

ammonium acetate. A gradient program was used to elute the IPU. After the analysis, the protonated molecular ion of IPU (*m/z* 207) and the protonated molecular ion of betamethasone (*m/z* 393) were extracted from the chromatograms. By dividing the peak areas of IPU by the peak areas of betamethasone, area ratios were obtained to compensate variations during the analysis.

For the degradation products, the respective fragment ions (FI) were extracted from the chromatograms as well as the FI for the betamethasone. By dividing the peak areas of the different degradation compounds by the peak area of betamethasone, area ratios were obtained to compensate variations during analysis of the degradation compounds. In the present work, it is assumed that these are the kinetically significant contributions, as one can expect at least to a first approximation similar sensitivities for species with similar types of chemical groups.

2.5. Respirometric studies

The potential production of harmful by-products, and therefore the biodegradability, during the degradation of the aqueous IPU solution under UV radiation was analyzed using respirometric tests with activated sludge. This sludge was obtained from the aeration basin of a municipal wastewater treatment plant (Aquafin, Harelbeke, Belgium). In order to remove remaining nutrients in the sample, the sludge was aerated for at least 24 hours and washed three times. This was done by letting the sludge settle for 10 minutes, removing the supernatant and adding tap water. Afterwards, 0.5 L of the settled sludge was added to the respirometric unit, together with glucose (mass concentration of 75 mg L^{-1}), NH_4Cl (mass concentration of 86.0 mg L^{-1}), KH_2PO_4 (mass concentration 16.5 mg L^{-1}), and 1 L of the (irradiated, thus treated) IPU solution. A neutral pH was reached prior to testing. The tests were performed with 5 and 10 mg aqueous

IPU solution, which experienced irradiation times of 4, 6, 8, and 16 hours, with tap water as reference (no irradiation counterpart).

The respirometric unit, in line with Manhaeghe *et al.* [78], consists of an open 2 L heat-jacketed reactor that allows for temperature control at 20°C. The reactor was stirred at 250 rpm (IKA Eurostar power control visc) to mimic a homogeneous suspension. The dissolved oxygen mass concentration (c_{O_2}; g O_2 m^{-3}) was measured online using an oxygen probe (Inpro 6860 i/12/120/nA, Mettler Toledo) that was connected to the Mettler Toledo M300 Multi 2 Channel 1/2 DIN transmitter. Using a Cole-Parmer 18200-00 data acquisition card and the software Instacal (Measurement Computing), the data was logged in LABVIEW (National Instruments). The oxygen uptake mass rate (OUR) (g O_2 $m^{-3}h^{-1}$) of the activated sludge is defined as:

$$OUR := \left|\frac{dc_{O_2}}{dt} - OTR\right| \quad (2)$$

in which the correction term denoted as OTR (g O_2 $m^{-3}h^{-1}$) is the oxygen mass transfer rate as defined between the liquid in the reactor vessel and the surrounding air of the open reactor vessel in case the air supply is closed. As shown in the Supporting Information (**Fig S6**), its relevance is limited but follows from:

$$OTR = K_{L,a}(c_{O_2} - c_{O_2,sat}) \quad (3)$$

in which the overall mass transfer coefficient between the surrounding air and the liquid in the reactor $K_{L,a}$ is 0.68 h^{-1} at 20°C [76] and $c_{O_2,sat}$ is the saturated oxygen mass concentration in the air (g O_2 m^{-3}). The later concentration is temperature dependent and can be calculated according ACSE [79], with T the temperature in °C [80]:

$$c_{O_2,sat} = 14.65 - 0.41T + 7.99\,10^{-3}T^2 - 7.78\,10^{-5}T^3 \quad (4)$$

3. Kinetic modelling methods

3.1. Kinetic Monte Carlo modelling for absolute concentration changes

For the calculation of the temporal evolution of the absolute concentrations for a degradation reaction scheme with several generations (e.g. **Fig 2** with four generations each time connected by three reaction pathways based on the assumption of unimolecular reactions and so ultimately 27 degradation products), kinetic Monte Carlo (*k*MC) simulations can be employed. Such simulations are free from issues due to stiffness or matrix inversions provided that a sufficiently large number of initial molecules is selected.

In the present work, the algorithm as developed by Gillespie [81,82] and as frequently applied for the stochastic description of polymerization processes is considered [83–85]. In this algorithm, the time evolution of a reactive system, as represented by a vector **X** containing the numbers of all species types in the sample volume, is followed. The associated reaction rates (total number *N*) are represented by the vector **a**. In the present work, upon initialization of **X** only the initial number of A (IPU) molecules possesses a non-zero value. This number needs to be sufficiently high to enable reliable stochastic sampling through two random numbers r_1 and r_2. The first number determines the time step τ between two reaction events (and is inversely proportional to the overall reaction rate) and the reaction "channel" μ is defined via the second random number r_2.

$$\tau = \frac{1}{\sum_{j=1}^{N} a(\boldsymbol{X})} \ln\left(\frac{1}{r_1}\right) \tag{5}$$

$$\sum_{j=1}^{\mu-1} a(\boldsymbol{X}) \leq r_2 \leq \sum_{j=1}^{\mu} a(\boldsymbol{X}) \tag{6}$$

Once the reaction type has been selected, the numbers in the stochastic volume and thus **X** are updated (with the associated update of **a**) and the sampling process is repeated until each reaction rate becomes zero or the user end-time is reached.

3.2. Simplified degradation kinetics based on quasi-steady-state approximation

In many chemical engineering processes with reactive intermediates the (molar) concentrations are approximated by making use of the quasi-steady-state-approximation (QSSA). For **Fig 2** (with three reactions connecting two generations) this means that formally the derivatives for the concentration change of the two intermediate types (B and C) are taken equal to zero. This implies for the concentration change of e.g. B_1 and C_{11} (no volume changes):

$$\frac{d[B_1]}{dt} = 0 = k_1[A] - (k_{11} + k_{12} + k_{13})[B_1] \tag{7}$$

$$\frac{d[C_{11}]}{dt} = 0 = k_{11}[B_1] - (k_{111} + k_{112} + k_{113})[C_{11}] \tag{8}$$

Taking into account that:

$$\frac{d[A]}{dt} = -(k_1 + k_2 + k_3)[A] \tag{9}$$

it follows that

$$[B_1] = \frac{k_1}{k_{11}+k_{12}+k_{13}}[A]_0 e^{-(k_1+k_2+k_3)t} \tag{10}$$

$$[C_{11}] = \frac{k_{11}}{k_{111}+k_{112}+k_{113}}[B_1] \tag{11}$$

with perturbations leading to the equations for the other products in **Fig 2**.

For the last generation in **Fig 2** (e.g. D_{111}) Eq. (10)-(11) imply:

$$\frac{d[D_{111}]}{dt} = k_{111}[C_{11}] = k_{111}\left(\frac{k_{11}}{k_{111}+k_{112}+k_{113}}\right)\left(\frac{k_1}{k_{11}+k_{12}+k_{13}}\right)[A]_0 e^{-(k_1+k_2+k_3)t} \quad (12)$$

which upon integration leads to:

$$[D_{111}] = [A]_0\left(\frac{k_1}{k_1+k_2+k_3}\right)\left(\frac{k_{11}}{k_{11}+k_{12}+k_{13}}\right)\left(\frac{k_{111}}{k_{111}+k_{112}+k_{113}}\right)\left(1 - e^{-(k_1+k_2+k_3)t}\right) \quad (13)$$

For a degradation reaction scheme still consisting of four generations but with the maximal number of reactions being a variable, e.g. $n_{max,l}$ (l=1, 2, 3) reactions per two generations, extrapolation allows to state the following concentration dependencies:

$$[A] = [A]_0 e^{-\left(\sum_{u=1}^{u=n_{max,1}} k_u\right)t} \quad (14)$$

$$[B_i] = [A]_0 \frac{k_i}{\sum_{v=1}^{v=n_{max,2}} k_{iv}} e^{-\sum_{u=1}^{u=n_{max,1}} k_u t} \quad (15)$$

$$\left[C_{ij}\right] = [A]_0 \frac{k_i}{\sum_{u=1}^{u=n_{max,1}} u} \frac{k_{ij}}{\sum_{v=1}^{v=n_{max,2}} k_{iv}} e^{-\left(\sum_{u=1}^{u=n_{max,1}} k_u\right)t} \quad (16)$$

$$\left[D_{ijk}\right] = [A]_0 \frac{k_i}{\sum_{u=1}^{u=n_{max,1}} k_u} \frac{k_{ij}}{\sum_{v=1}^{v=n_{max,2}} k_{iv}} \frac{k_{ijk}}{\sum_{w=1}^{3} k_{ijw}} \left(1 - e^{-\left(\sum_{u=1}^{u=n_{max,1}} k_u\right)t}\right) \quad (17)$$

For completeness, it is mentioned here that in Section **S3** and **S4** of the Supporting Information, a complete derivation, starting from single reactions ($n_{max,l}$=1) as reference case, is given for three (l=1,2) and four generations (l=1,2,3).

4. Results and discussion

4.1. Photocatalytic performance of dip-coated electrospun silica membranes with TiO_2 nanoparticles

The influence of the dip-coating process on the morphology and the catalytic performance of TiO_2 functionalized silica nanofibrous membranes has been studied in order to determine the optimal treatment of the silica-based heterogeneous photocatalyst. Both hydrophobic and superhydrophilic silica nanofibrous membranes have been tested. In this way, the influence of the water absorbing/repellent nature on the functionalization and photocatalytic degradation is investigated. Focus is on the variation of the TiO_2 loading and not the diameter range as the former can expected to be more dominant. Therefore, optimized parameters for the most constant fiber diameter are used for the electrospinning process.

Since the TiO_2 nanoparticles are dissolved in distilled water for the dip-coating process, the amount of particles onto the hydrophilic membranes is significantly higher than the hydrophobic one, as demonstrated in the SEM images of **Fig 3**. In addition, it is clear that particles are not just on top of the membrane, but mainly embedded inside the pores in between the fibers thus not significantly affecting the thickness. TiO_2 coatings were applied with three suspensions with different initial molar concentrations ($[TiO_2]_0$= 0.05, 0.34 and 0.50 mol L^{-1}) at two coating speeds (v= 80 and 160 mm min^{-1}). An overview of all TiO_2 coatings studied is given in **Fig S1** of the Supporting Information. The average diameter of the silica nanofibers is 348 ± 95 nm. Blockage of the pores due to TiO_2 nanoparticles stays limited, with a clean water permeability (CWP) that remains above 11.7 x 10^4 L $m^{-2}h^{-1}bar^{-1}$, which is in line with other state-of-the-art investigated nanofibrous membranes [86–88].

A quantification of the amount of TiO_2 on the membranes with ICP-OES and XRD indicates that the coatings with a 0.34 mol L^{-1} TiO_2 solution at 160 mm min^{-1} and a 0.50 mol L^{-1} solution at 80 mm min^{-1} have the highest loading, and thus have the highest potential as optimal coating for the photocatalytic degradation of IPU (**Table 2**; left panel). The amount of active sites available is of utmost importance, so a homogeneous distribution of the particles without large clusters on the fibers is crucial. This was confirmed with SEM for all dip-coated hydrophilic membranes, see example in **Fig 3**.

4.2. Conventional analysis of isoproturon degradation

Photocatalytic degradation experiments of IPU have been performed as described in Section 2.4. As shown in **Fig 4**, using UV-Vis spectroscopy, the concentration of the UV active IPU and its subsequent degradation products has been followed in a first step as a function of time for an aqueous solution with an initial mass concentration of 5 mg L^{-1} IPU in the presence of the 6 different TiO_2 functionalized silica nanofibrous membranes (first 6 entries in **Table 2**) and compared to the photolysis of IPU itself, hence, the case without the presence of a membrane.

Table 2. Left panel: Quantification of the TiO_2 loading on various dip-coated silica nanofibrous membranes determined via ICP-OES and XRD (CA: contact angle; $[TiO_2]_0$: initial molar concentration of the solution used for dip-coating; v: coating speed). Supported by the SEM analysis in Fig 3, the bold conditions (hydrophilic; 0.34 mol L^{-1}; 160 mm min^{-1}) seem the most promising for photocatalytic degradation of IPU. Right panel: first generation overall degradation rate coefficients of aqueous IPU solutions ($c_{IPU,0}$: initial mass concentration) in contact with various TiO_2 functionalized silica nanofibers (formally unimolecular reactions). These are determined based on the logarithmic plots in Fig 5a (Eq. (1)), using the IPU concentrations measured with LC-MS during the first 180 minutes of the experiment. The highest *k* values indeed result from the bold conditions.

Type of membrane			ICP-OES	XRD	$c_{IPU,0}$	*k*
CA	$[TiO_2]_0$	v (mm min^{-1})	(mg TiO_2)	(mg TiO_2)	(mg L^{-1})	(s^{-1})
145	0.34	80	0.25	0.38	5	$3 \pm 0.1\ 10^{-5}$
< 5	0.05	80	1.03	1.32	5	-
< 5	0.34	80	3.51	4.77	5	$1 \pm 0.01\ 10^{-4}$
< 5	**0.34**	**160**	**3.70**	**4.82**	**5**	**$2 \pm 0.1\ 10^{-4}$**
< 5	0.50	80	4.66	5.76	5	$9 \pm 0.5\ 10^{-5}$
< 5	0.50	160	3.16	5.91	5	$4 \pm 0.3\ 10^{-5}$
< 5	**0.34**	**160**	**3.70**	**4.82**	**10**	**$2 \pm 0.6\ 10^{-4}$**

It follows from **Fig 4** that the photolysis of IPU is limited, with even after 24 hours of irradiation less than 10% removed. The hydrophobic membrane results in a significant slower degradation of IPU compared to the superhydrophilic membranes, due to its water repellent nature combined with a lower TiO_2 loading (*cf.* interpretation of the left panel of **Table 2**). The 5 hydrpohilic silica membranes show a comparable trend, with a positive distinction of the fastest degradation for the coating with a 0.34 mol L^{-1} TiO_2 solution at coating speed of 160 mm min^{-1} (bold conditions in **Table 2**). SEM confirms a good distribution of the TiO_2 nanoparticles using this coating conditions (**Fig 3c**).

Typically, the photocatalytic degradation kinetics of IPU are formally described by a pseudo first-order rate law (**Eq. (1)**), and therefore in a second step – based on LC-MS results (**Fig 5a**) – the overall first generation photocatalytic activities have been calculated from the logarithmic plots of the pseudo first-order degradation rates of the IPU solution in contact with the TiO_2 functionalized membranes to determine the relative amount of only IPU in the solution after irradiation for varying time [55,58–60]. The resulting rate coefficients (formally unimolecular reactions) are given in **Table 2**, right panel. By using a superhydrophilic silica membrane according the optimized conditions, the highest degradation rate coefficient is achieved, namely 2.10^{-4} s^{-1} as confirmed for both 5 and 10 mg L^{-1} IPU solution. For this best set of coating conditions, the changes in mass concentration of IPU as a function of time measured with LC-MS are additionally given in **Fig 5b**. Both for the 5 and 10 mg L^{-1} IPU solution, IPU could no longer be detected after 8 hours of irradiation, and a half-life of less than 2 hours is observed, highlighting the consistency of the experimental analysis.

4.3. Kinetic analysis of multiple generations of degradation products

The kinetics and mechanisms for multiple generations of degradation products, starting from IPU, have been studied in a third step, again focusing on the optimal conditions determined in **Fig 4** (*cf.* interpretation of **Table 2**; bold conditions). By irradiating an aqueous IPU solution with UV light a complex solution of multiple degradation products is formed and a sole focus on the disappearance of IPU is thus not recommended.

For illustration purposes, a gradual degradation with four generations forming each time three degradation products has already been depicted in **Fig 2**. Similarly, various reaction intermediates and generations of them have been proposed in literature, based on LC-MS(-MS) analysis, and thus variations in the mass-charge ratios (*m/z* values) [66–72]. A detailed overview of the proposed intermediate products is given in **Fig S3** in the Supporting Information, with examples of associated chemical structures in **Fig S4** in the Supporting Information. As shown in **Fig 6**, essentially one has (i) hydroxylation on e.g. the isopropyl group, the dimethylamine group and the aromatic ring resulting in mono- and di-hydroxylated intermediates and eventually their oxidized products; (ii) N-demethylation or oxidation of amino groups linked to the benzene ring; (iii) methyl substitution; and (iv) isopropyl substitution. Combined, the reactions gradually result in mineralization of the herbicide.

To verify the possible existence of several generations of degradation products and the related reactions, LC-MS measurements have been performed in the present work by sampling the irradiated solution at regular time intervals and mapping the four generations of degradation products as introduced in **Fig 6**. Of the four main degradation products of the first generation in **Fig 6**, hydroxylation of IPU (*m/z* of 223; left box) yielded significantly higher signals than the ions with *m/z* 181, 193 and 209. It should be noted that the latter three were only detectable

after the injection of at least 20 times more sample, see recorded signals in **Fig S5** in the Supporting Information. This allows at least for a first approximation to associate the connectivity of the first and second generation by only hydroxylation. Supported by a careful scanning of the global MS spectrum, still bearing in mind possible sensitivity differences, this dominance of hydroxylation reactions can be generalized to the other generations. In the simplified representation, as depicted by the grey boxes in **Fig 6**, the relative appearances and disappearances of molecules/intermediates formed by consecutive hydroxylation reactions are only covered, with the *m/z* of the formed intermediates being 223 (product of generation 1), 239 (product of generation 2), and 255 (product of generation 3).

The corresponding relative concentration changes (normalized based on the maximum value) are provided in **Fig 7a-c**. It follows that starting from IPU (*A*), respectively three ($B_{1\text{-}3}$), two ($C_{1,2}$) and again two ($D_{1,2}$) degradation product types can be detected for the subsequent generations. In all cases, the intermediates are detected at distinct retention times, indicating different hydroxylated molecular forms, consistent with the exemplary chemical molecules in **Fig 6** and **Fig S4** in the Supporting Information. It is observed that once the IPU reacts on the surface of the TiO_2 nanoparticles (first generation product), further hydroxylation (higher order generation products) occurs sufficiently fast.

These experimental observations can be further interpreted based on *k*MC simulations (based on **Eq. (5)-(6)**) , as shown in **Fig 7** (middle row). The simulation lines mimic only similar trends as in **Fig 7** (top row) and need to be interpreted in a qualitative manner, with the tuned rate coefficients listed in **Table 3**. For this parameter tuning it is assumed that one has for each generation (after the first generation consisting of the starting product *A*; IPU) formally three species types (*cf.* **Fig 2**), based on the experimental observation that at the start of the

degradation process three *B* types are detected. At first sight this seems an issue as later on experimentally only two *C* and *D* types are detected (top row of **Fig 7**). It should however be realized that hydroxylation can take place at several locations on the molecular level and thus the same product can be made in several ways. For example, the same third generation product results for the order hydroxylation on the isopropyl group and the benzene ring as the order hydroxylation on the benzene ring and the isopropyl group.

In **Table 3,** the rate coefficients k_1, k_2 and k_3 represent therefore hydroxylations at three different locations on the molecule. Their sum is notably similar to the overall degradation coefficient based on conventional analysis (value of 2.10^{-4} s^{-1} in **Table 2**), highlighting the overall consistency of the experimental and theoretical framework. In this table, k_1 and k_3 are repeated for other generations to highlight patterns of identical product formation, as explained above. The last three rate coefficients in the table are formally introduced to enable a disappearance of *D* intermediates toward the next generation (*E*), which is although not explicitly detected experimentally. Only the decay of *D* species is experimentally mapped, which is sufficient to allow for an assessment of the last three parameters. For simplicity, a single scaling factor with respect to k_1 is considered.

Overall it follows that the modeling results (**Fig 7**; middle row) are in agreement with the experimental results (**Fig 7**; top row). This further supports the research hypothesis that consecutive hydroxylation reactions are dominant in the degradation of IPU. It should be additionally noted that a simulation based on QSSA can be biased (theoretical equations see **Eq. (7)-(17)**). As shown in the bottom row of **Fig 7** – utilizing the rate coefficients as tuned based on the detailed kMC model - only the final degradation times per transition (depletion of intermediates) can be assessed but not the actual shape of the concentration distributions.

Table 3. Tuned rate coefficients to describe the degradation kinetics of IPU through kinetic Monte Carlo simulations considering several generations. The dominant hydroxylation reaction pathways from Fig 6 (grey boxes) are selected. Generations are abbreviated as *A*, *B*, *C*, *D* and *E*, with *A* being IPU; rate coefficients defined *cf.* Fig 2; the experimental results (Fig 7; top row) indicate that one apparently goes from three detectable *B* species types to two detectable *C* and two *D* types. As consecutive hydroxylation is assumed, identical species can be obtained if the order of the location of the first and second hydroxylation is altered (e.g. sequence isopropyl group/benzene ring gives the same result as the sequence benzene ring/isopropyl group).[a]

from	to	k	value (s^{-1})
A	B_1	k_1 [b]	$1.2\ 10^{-4}$
A	B_2	k_2 [b]	$1.1\ 10^{-4}$
A	B_3	k_3 [b]	$7.0\ 10^{-5}$
B_1	C_{11}	k_{11}	$k_{11} = k_3$
B_2	C_{21}	k_{21}	$k_{21} = k_1$
B_3	C_{31}	k_{31}	$k_{31} = k_1$
C_{11}	D_{111}	k_{111}	$k_{111} = k_1$
C_{21}	D_{211}	k_{211}	$k_{211} = k_3$
C_{31}	D_{311}	k_{311}	$k_{311} = k_1$
D_{111}	E_{1111}	k_{1111}	$10\ k_1$
D_{211}	E_{2111}	k_{2111}	$10\ k_1$
D_{311}	E_{3111}	k_{3111}	$10\ k_1$

[a] The experimental concentration for C_1 is the sum of the simulated concentration for C_{11} and C_{31} as they are assumed to be identical species; the experimental concentration for C_2 is taken as the simulated concentration for C_{21}; similarly the experimental concentration for D_1 is the sum of the simulated concentration for D_{111} and D_{311}; the experimental concentration for D_2 is taken as the one for D_{211}.

[b] These three rate coefficients correspond to three locations for the hydroxylation.

4.4. Catalyst reusability and quantification of the toxicity

The recyclability and stability in time of the photocatalyst are essential for the practical relevance. Therefore, initial testing of the structural stability of a functionalized silica nanofibrous membrane (optimal conditions **Table 2**) was tested by cyclic testing for 5 times, using a IPU solution with initial mass concentration of 5 mg L^{-1} which was irradiated for 8 hours (**Fig 8)**. Even after 5 cycles, the degradation of UV active species remains high, with a removal above 90% after 8 hours of irradiation, indicating an excellent reusability of the photocatalytic nanofibrous membrane. In addition, the membrane preserves its good structural integrity and mechanical stability, avoiding an additional separation step of the photocatalytic active component in comparison with the use of the TiO_2 nanoparticles without carrier material

(see **Fig S6** in the Supporting Information) [70,89–92]. However, more prolonged durability studies on a pilot scale setup are required in future work to support these data.

Another important aspect is the influence of the UV irradiation of the IPU solution on the environment when reintroduced into the surface water after the treatment or when introduced in conventional municipal waste water treatment. We aim for a decreased toxicity, where the biological environment experiences less negative effects of the agricultural herbicides compared to a non-treated IPU solution. This is an aspect lacking in the conventional techniques used for the removal of pesticides from water (e.g. reverse osmosis and adsorption using granular activated carbon). An indicative technique that can be used is respirometry. This method measures the consumption rate of O_2 of an activated sludge and translates this into an oxygen uptake rate (OUR; **Eq. (2)-(4)**), which then can be coupled to the kinetics of the organisms [80].

A representation of the measurement is given in **Fig 9**. In a cooled open reactor vessel, 0.5 L of washed activated sludge is mixed with 1 L of the tested solution, in addition with glucose, NH_4Cl and KH_2PO_4 to avoid limitations in the growth due to shortage of N and P in the reactor vessel (**Fig 9a**). An oxygen probe is inserted in the vessel to follow the oxygen consumption of the activated sludge as a measureable effect of the glucose conversion. To allow multiple tests of the same solution, air was pumped in the reactor once the O_2 level went below 2 mg O_2 L^{-1}. This was repeated twice, resulting in the oxygen levels as indicated in **Fig 9b** (example of blank and untreated 5 mg L^{-1} IPU solution (no irradiation)). The faster the consumption of O_2, the less inhibition of the activated sludge by the tested solution, and thus resulting in less influence of the solution upon reintroducing it in the environment. By using **Eq. (2)**, the recorded data can be converted elegantly to the averaged OUR of the activated sludge for each of the three

measurements, see **Fig 9c** as proof of principle for the blank solution. The influence of the value of $K_{L,a}$ on the OUR value is given in **Fig S7** in the Supporting Information for the solutions in **Fig 9b**, illustrating that even though the absolute values are slightly altered, the trend is not changed by deviating $K_{L,a}$.

In a final step, respirometric studies were thus performed with IPU solutions with mass concentration of 5 and 10 mg L^{-1} without treatment, and after UV irradiation for 4, 6, 8 and 16 hours to study the influence of the irradiation time. Starting from the blank solution and switching to the 5 mg L^{-1} IPU solutions, a gradual increase of the OUR with increasing UV irradiation time can be observed, see **Fig 10a**, where the OUR values of the first slopes of **Fig 9b** are given. An irradiation of 6 hours shows a slight deviation from this trend, suggesting the temporarily formation of intermediate product(s) that hinder the oxygen uptake of the activated sludge, and therefore suggesting that prolonged irradiation time of the IPU contaminated solutions is desired. Overall, irradiation for more than 8 hours results in an increase in OUR, comparable to the reference solution, see **Fig 10b** where the average OUR values of the references and 8 and 16 hours treated solutions for the first O_2 consumption measurement are given. It follows from the guidelines for the eye that a significant inhibition of the activated sludge is observed if IPU is present. This can be prevented by a priori irradiation with UV light, leading to an OUR of the same order of magnitude as the blank solution. A complete overview of all measurements is given in **Fig S8** of the Supporting Information. Combining this with the results in Section 4.3 shows a relatively small molecular change, as hydroxylation of the IPU molecules, allows for a decreased influence on the activity of the activated sludge. In other words, if complete removal using photocatalysis cannot be achieved, the overall goal of reducing the environmental influence of isoproturon use in amongst others agriculture is achieved.

5. Conclusions

The photocatalytic degradation of aqueous isoproturon (IPU) solutions in the presence of TiO_2 functionalized silica nanofibrous membranes has been studied. An efficient, reusable heterogeneous catalyst is obtained when dip-coating the nanofibers with an aqueous nanoparticle suspension (0.34 mol L^{-1} of TiO_2) at high dip-coating speed (160 mm min^{-1}), without loss in catalytic activity after 5 cycles. This designed combination of coating solution and speed results in a homogeneous distribution of the particles without significant clustering, allowing for a large available surface area of TiO_2. This optimal coating enables complete IPU removal from a solution with mass concentrations of 5 and 10 mg L^{-1} in less than 8 hours.

Three additional generations of products could be detected based on LC-MS. Of the four main degradation reactions (hydroxylation, N-demethylation, methyl substitution, and isopropyl substitution), hydroxylation reactions are observed in considerable higher concentrations and occurring at different locations on the molecule with eventually intermediates possessing an identical structure due to a switch of the order of the locations. Once the reaction of IPU at the TiO_2 surface is initiated, the next generations of the degradation process are encountered sufficiently fast as additionally confirmed by kinetic Monte Carlo simulations.

A quantitative study of the decreased toxicity of the IPU solution after UV-treatment has also been performed using respirometry with activated sludge as indicative technique. By UV-treatment the oxygen uptake rate of the activated sludge is increased significantly (6.2 ± 0.6 mg O_2 $g_{activated\ sludge}^{-1}h^{-1}$ for a 5 mg L^{-1} IPU solution before irradiation vs. 8.7 ± 0.3 mg O_2 $g_{activated\ sludge}^{-1}h^{-1}$ after 8 hours of irradiation). This means that the activated sludge is not inhibited anymore by the irradiated IPU solution, allowing to safely discharge the liquid

into the environment, and proving the potential of this technique as an alternative for pressure driven reverse osmosis or the adsorption of the pesticide using granular activated carbon.

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Notation

[ ]	molar concentration, mol L^{-1}
c	mass concentration, g L^{-1}
k	degradation rate coefficient, s^{-1}
$K_{L,a}$	overall mass transfer coefficient, h^{-1}
m/z	mass-charge ratio
t	time, s
v	coating speed, mm min^{-1}

Abbrevations

AOP	advanced oxidation process
CE	collision energy
CWP	clean water permeability
FI	fragment ion

HT heat treatment

ICP-OES inductively coupled plasma optical emission spectroscopy

IPU isoproturon

*k*MC kinetic Monte Carlo

LC-MS liquid chromatography – mass spectrometry

OTR oxygen transfer rate

OUR oxygen uptake rate

PI precursor ion

QSSA quasi-steady-state approximation

TEOS tetraethyl orthosilicate

UV ultra-violet

XRD x-ray diffraction

References

[1] W.-W. Li, H. Yu, B.E. Rittmann, Reuse water pollutants, Nature. 528 (2015) 29–31. doi:10.1038/528029a.

[2] D. Bixio, C. Thoeye, J. De Koning, D. Joksimovic, D. Savic, Wastewater reuse in Europe, Desalination. 187 (2006) 89–101. doi:10.1016/j.desal.2005.04.070.

[3] T.A. Larsen, S. Hoffmann, B. Truffer, M. Maurer, Emerging solutions to the water challenges of an urbanizing world, Science. 352 (2016) 928–933. doi:10.1126/science.aad8641.

[4] T. Fotiou, T.M. Triantis, T. Kaloudis, A. Hiskia, Evaluation of the photocatalytic activity of TiO_2 based catalysts for the degradation and mineralization of cyanobacterial toxins and water off-odor compounds under UV-A, solar and visible light, Chem. Eng. J. 261 (2015) 17–26. doi:10.1016/j.cej.2014.03.095.

[5] I. Losito, A. Amorisco, F. Palmisano, P.G. Zambonin, X-ray photoelectron spectroscopy characterization of composite TiO_2-poly(vinylidenefluoride) films synthesised for applications in pesticide photocatalytic degradation, Appl. Surf. Sci. 240 (2005) 180–188. doi:10.1016/j.apsusc.2004.06.068.

[6] G. Boczkaj, A. Fernandes, Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review, Chem. Eng. J. 320 (2017) 608–633. doi:10.1016/j.cej.2017.03.084.

[7] R. Dewil, D. Mantzavinos, I. Poulios, M.A. Rodrigo, New perspectives for Advanced Oxidation Processes, J. Environ. Manage. 195 (2017) 93–99. doi:10.1016/j.jenvman.2017.04.010.

[8] A.R. Ribeiro, O.C. Nunes, M.F.R. Pereira, A.M.T. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, Environ. Int. 75 (2015) 33–51. doi:10.1016/j.envint.2014.10.027.

[9] Y. Yang, J.J. Pignatello, J. Ma, W.A. Mitch, Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs), Environ. Sci. Technol. 48 (2014) 2344–2351. doi:10.1021/es404118q.

[10] F. Sopaj, M.A. Rodrigo, N. Oturan, F.I. Podvorica, J. Pinson, M.A. Oturan, Influence of the anode materials on the electrochemical oxidation efficiency. Application to oxidative degradation of the pharmaceutical amoxicillin, Chem. Eng. J. 262 (2015) 286–294. doi:10.1016/j.cej.2014.09.100.

[11] M. V. Phanikrishna Sharma, V. Durga Kumari, M. Subrahmanyam, TiO_2 supported over porous silica photocatalysts for pesticide degradation using solar light: Part 2. Silica prepared using acrylic acid emulsion, J. Hazard. Mater. 175 (2010) 1101–1105. doi:10.1016/j.jhazmat.2009.10.056.

[12] M. V. Phanikrishna Sharma, V. Durga Kumari, M. Subrahmanyam, Photocatalytic degradation of isoproturon herbicide over TiO_2/Al-MCM-41 composite systems using solar light, Chemosphere. 72 (2008) 644–651. doi:10.1016/j.chemosphere.2008.02.042.

[13] I.K. Konstantinou, V.A. Sakkas, T.A. Albanis, Photocatalytic degradation of propachlor in aqueous TiO_2 suspensions. Determination of the reaction pathway and identification of intermediate products by various analytical methods, Water Res. 36 (2002) 2733–2742. doi:10.1016/S0043-1354(01)00505-X.

[14] M. Muneer, M. Qamar, M. Saquib, D.W. Bahnemann, Heterogeneous photocatalysed reaction of three selected pesticide derivatives, propham, propachlor and tebuthiuron in aqueous suspensions of titanium dioxide, Chemosphere. 61 (2005) 457–468. doi:10.1016/j.chemosphere.2005.03.006.

[15] C.D.S. Tomlin, The pesticide manual: A World compedium, 11th ed., British Crop Production Council, Alton, 2009.

[16] G.D. Bending, S.D. Lincoln, R.N. Edmondson, Spatial variation in the degradation rate of the pesticides isoproturon, azoxystrobin and diflufenican in soil and its relationship with chemical and microbial properties, Environ. Pollut. 139 (2006) 279–287. doi:10.1016/j.envpol.2005.05.011.

[17] S. Issa, M. Wood, Degradation of atrazine and isoproturon in surface and sub-surface soil materials undergoing different moisture and aeration conditions, Pest Manag. Sci. 61 (2005) 126–132. doi:10.1002/ps.951.

[18] R.H. Coupe, J.D. Blomquist, Water-soluble pesticides in finished water of community water supplies, Am. Water Work. Assoc. 96 (2004) 56–68. http://www.jstor.org/stable/41311234.

[19] A. Verma, N.T. Prakash, A.P. Toor, An efficient TiO_2 coated immobilized system for the degradation studies of herbicide isoproturon: Durability studies, Chemosphere. 109 (2014) 7–13. doi:10.1016/j.chemosphere.2014.02.051.

[20] S. Ahmed, M.G. Rasul, R. Brown, M.A. Hashib, Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review, J. Environ. Manage. 92 (2011) 311–330. doi:10.1016/j.jenvman.2010.08.028.

[21] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, Appl. Catal. B Environ. 202 (2017) 217–261. doi:10.1016/j.apcatb.2016.08.037.

[22] M.R. Espino-Estévez, C. Fernández-Rodríguez, O.M. González-Díaz, J.A. Navío, D. Fernández-Hevia, J.M. Doña-Rodríguez, Enhancement of stability and photoactivity of TiO2 coatings on annular glass reactors to remove emerging pollutants from waters, Chem. Eng. J. 279 (2015) 488–497. doi:10.1016/j.cej.2015.05.038.

[23] S. Parra, S. Malato, C. Pulgarin, New integrated photocatalytic-biological flow system using supported TiO_2 and fixed bacteria for the mineralization of isoproturon, Appl. Catal. B Environ. 36 (2002) 131–144. doi:10.1016/S0926-3373(01)00293-4.

[24] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47 (2013) 3931–3946. doi:10.1016/j.watres.2012.09.058.

[25] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipe, J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification, Appl. Catal. B Environ. 7 (1995) 49–63. doi:10.1016/0926-3373(95)00026-7.

[26] B. Srikanth, R. Goutham, R. Badri Narayan, A. Ramprasath, K.P. Gopinath, A.R. Sankaranarayanan, Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment, J. Environ. Manage. 200 (2017) 60–78. doi:10.1016/j.jenvman.2017.05.063.

[27] S. Singh, H. Mahalingam, P.K. Singh, Polymer-supported titanium dioxide photocatalysts for environmental remediation: A review, Appl. Catal. A Gen. 462–463 (2013) 178–195. doi:10.1016/j.apcata.2013.04.039.

[28] H. Dong, G. Zeng, L. Tang, C. Fan, An overview on limitations of TiO_2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures, Water Res. 79 (2015) 128–146. doi:10.1016/j.watres.2015.04.038.

[29] Z. Shayegan, C.S. Lee, F. Haghighat, TiO2 photocatalyst for removal of volatile organic compounds in gas phase – A review, Chem. Eng. J. 334 (2018) 2408–2439. doi:10.1016/j.cej.2017.09.153.

[30] A.H. Mamaghani, F. Haghighat, C.S. Lee, Photocatalytic oxidation technology for indoor environment air purification: The state-of-the-art, Appl. Catal. B Environ. 203 (2017) 247–269. doi:10.1016/j.apcatb.2016.10.037.

[31] H. Zangeneh, A.A.L. Zinatizadeh, M. Habibi, M. Akia, M.H. Isa, Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides : A comparative review, J. Ind. Eng. Chem. 26 (2015) 1–36. doi:10.1016/j.jiec.2014.10.043.

[32] C. Byrne, G. Subramanian, S.C. Pillai, Recent advances in photocatalysis for environmental applications, J. Environ. Chem. Eng. 6 (2018) 3531–3555. doi:10.1016/j.jece.2017.07.080.

[33] N. Shaham-waldmann, Y. Paz, Away from TiO_2 : A critical minireview on the developing of new photocatalysts for degradation of contaminants in water, Mater. Sci. Semicond. Process. 42 (2016) 72–80. doi:10.1016/j.mssp.2015.06.068.

[34] S. Dong, J. Feng, M. Fan, Y. Pi, L. Hu, X. Han, M. Liu, J. Sun, J. Sun, Recent developments in heterogeneous photocatalytic water treatment using visible light-responsive photocatalysts: a review, RSC Adv. 5 (2015) 14610–14630. doi:10.1039/C4RA13734E.

[35] E. Loccufier, J. Geltmeyer, L. Daelemans, D.R. D'hooge, K. De Buysser, K. De Clerck, Silica Nanofibrous Membranes for the Separation of Heterogeneous Azeotropes, Adv. Funct. Mater. 28 (2018) 1–10. doi:10.1002/201804138.

[36] S. Peng, G. Jin, L. Li, K. Li, M. Srinivasan, S. Ramakrishna, J. Chen, Multi-functional electrospun nanofibres for advances in tissue regeneration, energy conversion & storage, and water treatment, Chem. Soc. Rev. 45 (2016) 1225–1241. doi:10.1039/C5CS00777A.

[37] A. Greiner, J.H. Wendorff, Electrospinning: A fascinating method for the preparation of ultrathin fibers, Angew. Chemie - Int. Ed. 46 (2007) 5670–5703. doi:10.1002/anie.200604646.

[38] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications, Desalination. 356 (2015) 15–30.

doi:10.1016/j.desal.2014.09.033.

[39] S. Ramakrishna, K. Fujihara, W.E. Teo, T. Yong, Z. Ma, R. Ramaseshan, Electrospun nanofibers: Solving global issues, Mater. Today. 9 (2006) 40–50. doi:10.1016/S1369-7021(06)71389-X.

[40] K.M. Dobosz, C.A. Kuo-Leblanc, T.J. Martin, J.D. Schiffman, Ultrafiltration Membranes Enhanced with Electrospun Nanofibers Exhibit Improved Flux and Fouling Resistance, Ind. Eng. Chem. Res. 56 (2017) 5724–5733. doi:10.1021/acs.iecr.7b00631.

[41] J. Geltmeyer, H. Teixido, M. Meire, T. Van Acker, K. Deventer, F. Vanhaecke, S. Van Hulle, K. De Buysser, K. De Clerck, TiO2 functionalized nanofibrous membranes for removal of organic (micro)pollutants from water, Sep. Purif. Technol. 179 (2017) 533–541. doi:10.1016/j.seppur.2017.02.037.

[42] N. Daels, M. Radoicic, M. Radetic, S.W.H. Van Hulle, K. De Clerck, Functionalisation of electrospun polymer nanofibre membranes with TiO2 nanoparticles in view of dissolved organic matter photodegradation, Sep. Purif. Technol. 133 (2014) 282–290. doi:10.1016/j.seppur.2014.06.040.

[43] Y. Dai, W. Liu, E. Formo, Y. Sun, Y. Xia, Ceramic nanofibers fabricated by electrospinning and their applications in catalysis, environmental science, and energy technology, Polym. Adv. Technol. 22 (2011) 326–338. doi:10.1002/pat.1839.

[44] H. Esfahani, R. Jose, S. Ramakrishna, Electrospun ceramic nanofiber mats today: Synthesis, properties, and applications, Materials (Basel). 10 (2017). doi:10.3390/ma10111238.

[45] D. Li, Y. Xia, Direct fabrication of composite and ceramic hollow nanofibers by electrospinning, Nano Lett. 4 (2004) 933–938. doi:10.1021/nl049590f.

[46] D. Malwal, P. Gopinath, Efficient adsorption and antibacterial properties of electrospun CuO-ZnO composite nanofibers for water remediation, J. Hazard. Mater. 321 (2017) 611–621. doi:10.1016/j.jhazmat.2016.09.050.

[47] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, Water Res. 44 (2010) 2997–3027. doi:10.1016/j.watres.2010.02.039.

[48] J. Geltmeyer, L. Van Der Schueren, F. Goethals, K. De Buysser, K. De Clerck, Optimum sol viscosity for stable electrospinning of silica nanofibres, J. Sol-Gel Sci. Technol. 67 (2013) 188–195. doi:10.1007/s10971-013-3066-x.

[49] J. Geltmeyer, J. De Roo, F. Van den Broeck, J.C. Martins, K. De Buysser, K. De Clerck, The influence of tetraethoxysilane sol preparation on the electrospinning of silica nanofibers, J. Sol-Gel Sci. Technol. 77 (2016) 453–462. doi:10.1007/s10971-015-3875-1.

[50] S. Agarwal, A. Greiner, J.H. Wendorff, Functional materials by electrospinning of polymers, Prog. Polym. Sci. 38 (2013) 963–991.

doi:10.1016/j.progpolymsci.2013.02.001.

[51] D. Li, J.T. McCann, Y. Xia, M. Marquez, Electrospinning: A simple and versatile technique for producing ceramic nanofibers and nanotubes, J. Am. Ceram. Soc. 89 (2006) 1861–1869. doi:10.1111/j.1551-2916.2006.00989.x.

[52] L.T. Zhuravlev, The surface chemistry of amorphous silica. Zhuravlev model, Colloids Surfaces A Physicochem. Eng. Asp. 173 (2000) 1–38. doi:10.1016/S0927-7757(00)00556-2.

[53] L. Peng, W. Qisui, L. Xi, Z. Chaocan, Investigation of the states of water and OH groups on the surface of silica, Colloids Surfaces A Physicochem. Eng. Asp. 334 (2009) 112–115. doi:10.1016/j.colsurfa.2008.10.028.

[54] N. Hamzah, C.P. Leo, Membrane distillation of saline with phenolic compound using superhydrophobic PVDF membrane incorporated with TiO_2 nanoparticles: Separation, fouling and self-cleaning evaluation, Desalination. 418 (2017) 79–88. doi:10.1016/j.desal.2017.05.029.

[55] S. Ho, S. Kwak, B. Sohn, T. Hyun, Design of TiO_2 nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane as an approach to solve biofouling problem, Jorunal Membr. Sci. 211 (2003) 157–165.

[56] P. Gkotsis, D. Banti, E. Peleka, A. Zouboulis, P. Samaras, Fouling Issues in Membrane Bioreactors (MBRs) for Wastewater Treatment: Major Mechanisms, Prevention and Control Strategies, Processes. 2 (2014) 795–866. doi:10.3390/pr2040795.

[57] A.M. El-toni, S. Yin, T. Sato, T. Ghannam, M. Al-hoshan, M. Al-salhi, Investigation of photocatalytic activity and UV-shielding properties for silica coated titania nanoparticles by solvothermal coating, J. Alloys Compd. 508 (2010) L1–L4. doi:10.1016/j.jallcom.2010.08.031.

[58] I. Ahmed, T. Furusawa, M. Sato, K. Honda, Control of the photocatalytic activity of TiO2 nanoparticles by silica coating with polydiethoxysiloxane, 76 (2008) 754–759. doi:10.1016/j.dyepig.2007.01.020.

[59] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review, Appl. Catal. B Environ. 49 (2004) 1–14. doi:10.1016/j.apcatb.2003.11.010.

[60] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, Desalination. 261 (2010) 3–18. doi:10.1016/j.desal.2010.04.062.

[61] A.R. Khataee, M.N. Pons, O. Zahraa, Photocatalytic degradation of three azo dyes using immobilized TiO_2 nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure, J. Hazard. Mater. 168 (2009) 451–457. doi:10.1016/j.jhazmat.2009.02.052.

[62] P. García-mu, J. Carbajo, M. Faraldos, A. Bahamonde, Photocatalytic degradation of

phenol and isoproturon : Effect of adding an activated carbon to titania catalyst, J. Photochem. Photobiol. A Chem. 287 (2014) 8–18. doi:10.1016/j.jphotochem.2014.05.002.

[63] A. Alatrache, O. Zahraa, Degradation of the herbicide isoproturon by a photocatalytic process, Comptes Rendus Chim. 17 (2014) 824–831. doi:10.1016/j.crci.2014.04.002.

[64] M. V. Phanikrishna Sharma, G. Sadanandam, A. Ratnamala, V. Durga Kumari, M. Subrahmanyam, An efficient and novel porous nanosilica supported TiO_2 photocatalyst for pesticide degradation using solar light, J. Hazard. Mater. 171 (2009) 626–633. doi:10.1016/j.jhazmat.2009.06.040.

[65] M. V. Phanikrishna Sharma, V. Durga Kumari, M. Subrahmanyam, TiO_2 supported over SBA-15: An efficient photocatalyst for the pesticide degradation using solar light, Chemosphere. 73 (2008) 1562–1569. doi:10.1016/j.chemosphere.2008.07.081.

[66] A. Verma, N.T. Prakash, A. Pal, Photocatalytic Degradation of Herbicide Isoproturon in TiO2 Aqueous Suspensions: Study of Reaction Intermediates and Degradation Pathways, Environ. Prog. Sustain. Energy. 00 (2013). doi:10.1002/ep.

[67] M.V.P. Sharma, V.D. Kumari, M. Subrahmanyam, Photocatalytic degradation of isoproturon herbicide over TiO2 / Al-MCM-41 composite systems using solar light, Chemosphere. 72 (2008) 644–651. doi:10.1016/j.chemosphere.2008.02.042.

[68] M.M. Haque, M. Muneer, Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide, J. Environ. Manage. 69 (2003) 169–176. doi:10.1016/S0301-4797(03)00143-9.

[69] A. Amorisco, I. Losito, F. Palmisano, P.G. Zambonin, Photocatalytic degradation of the herbicide isoproturon: Characterisation of by-products by liquid chromatography with electrospray ionisation tandem mass spectrometry, Rapid Commun. Mass Spectrom. 19 (2005) 1507–1516. doi:10.1002/rcm.1950.

[70] I. Losito, A. Amorisco, F. Palmisano, Electro-Fenton and photocatalytic oxidation of phenyl-urea herbicides: An insight by liquid chromatography-electrospray ionization tandem mass spectrometry, Appl. Catal. B Environ. 79 (2008) 224–236. doi:10.1016/j.apcatb.2007.10.029.

[71] A. Revilla, J. Aguado, M.J. López-mu, Heterogeneous photocatalytic degradation of isoproturon in aqueous solution: Experimental design and intermediate products analysis, Catal. Today. 209 (2013) 99–107. doi:10.1016/j.cattod.2012.11.017.

[72] M.R. Espino-Estévez, C. Fernández-Rodríguez, O.M. González-Díaz, J. Araña, J.P. Espinós, J.A. Ortega-Méndez, J.M. Doña-Rodríguez, Effect of TiO_2-Pd and TiO_2-Ag on the photocatalytic oxidation of diclofenac, isoproturon and phenol, Chem. Eng. J. 298 (2016) 82–95. doi:10.1016/j.cej.2016.04.016.

[73] D.R. D'Hooge, P.H.M. Van Steenberge, M.F. Reyniers, G.B. Marin, The strength of multi-scale modeling to unveil the complexity of radical polymerization, Prog. Polym.

Sci. 58 (2016) 59–89. doi:10.1016/j.progpolymsci.2016.04.002.

[74] A. Nasresfahani, L.A. Idowu, R.A. Hutchinson, Extractable content of functional acrylic resins produced by radical copolymerization: A comparison of experiment and stochastic simulation, Chem. Eng. J. 378 (2019) 122087. doi:10.1016/j.cej.2019.122087.

[75] C. Bian, Y.N. Zhou, J.D. Deetz, Z.H. Luo, Experimental and computational investigation of oxidative quenching governed aqueous organocatalyzed atom transfer radical polymerization, Chem. Eng. J. 362 (2019) 721–730. doi:10.1016/j.cej.2019.01.087.

[76] D. Bjorge, N. Daels, S. De Vrieze, P. Dejans, T. Van Camp, W. Audenaert, J. Hogie, P. Westbroek, K. De Clerck, S.W.H. Van Hulle, Performance assessment of electrospun nanofibers for filter applications, Desalination. 249 (2009) 942–948. doi:10.1016/j.desal.2009.06.064.

[77] N. Daels, S. De Vrieze, I. Sampers, B. Decostere, P. Westbroek, A. Dumoulin, P. Dejans, K. De Clerck, S.W.H. Van Hulle, Potential of a functionalised nanofibre microfiltration membrane as an antibacterial water filter, Desalination. 275 (2011) 285–290. doi:10.1016/j.desal.2011.03.012.

[78] D. Manhaeghe, S. Michels, D.P.L. Rousseau, S.W.H. Van Hulle, A semi-mechanistic model describing the influence of light and temperature on the respiration and photosynthetic growth of Chlorella vulgaris, Bioresour. Technol. 274 (2019) 361–370. doi:10.1016/j.biortech.2018.11.097.

[79] A.S. of C. Engineers, Standard guidelines for in-process oxygen transfer testing, in: American Society of Civil Engineers, 2018.

[80] B. Decostere, N. Janssens, A. Alvarado, T. Maere, P. Goethals, S.W.H. Van Hulle, I. Nopens, A combined respirometer – titrimeter for the determination of microalgae kinetics : Experimental data collection and modelling, Chem. Eng. J. 222 (2013) 85–93. doi:10.1016/j.cej.2013.01.103.

[81] D.T. Gillespie, A general method for numerically simulating the stochastic time evolution of coupled chemical reactions, J. Comput. Phys. 22 (1976) 403–434. doi:10.1016/0021-9991(76)90041-3.

[82] D.T. Gillespie, Exact stochastic simulation of coupled chemical reactions, J. Phys. Chem. 81 (1977) 2340–2361. doi:10.1021/j100540a008.

[83] P.H.M. Van Steenberge, D.R. D'Hooge, Y. Wang, M. Zhong, M.F. Reyniers, D. Konkolewicz, K. Matyjaszewski, G.B. Marin, Linear gradient quality of ATRP copolymers, Macromolecules. 45 (2012) 8519–8531. doi:10.1021/ma3017597.

[84] S.K. Fierens, D.R. D'hooge, P.H.M. Van Steenberge, M.F. Reyniers, G.B. Marin, MAMA-SG1 initiated nitroxide mediated polymerization of styrene: From Arrhenius parameters to model-based design, Chem. Eng. J. 278 (2015) 407–420. doi:10.1016/j.cej.2014.09.024.

[85] C. Pinto, A.L.T. Brand, L. Alberton, When Polymer Reaction Engineers Play Dice:

Applications of Monte Carlo Models in PRE, Macromol. React. Eng. 9 (2015) 141–185. doi:10.1002/mren.201500020.

[86] J.-H. Choi, H.Y. Ng, Effect of membrane type and material on performance of a submerged membrane bioreactor, Chemosphere. 71 (2008) 853–859. doi:http://dx.doi.org/10.1016/j.chemosphere.2007.11.029.

[87] N.L. Le, S.P. Nunes, Materials and membrane technologies for water and energy sustainability, Sustain. Mater. Technol. 7 (2016) 1–28. doi:10.1016/j.susmat.2016.02.001.

[88] L.A. Goetz, N. Naseri, S.S. Nair, Z. Karim, A.P. Mathew, All cellulose electrospun water purification membranes nanotextured using cellulose nanocrystals, Cellulose. 25 (2018) 3011–3023. doi:10.1007/s10570-018-1751-1.

[89] J. Song, X. Wang, J. Yan, J. Yu, G. Sun, B. Ding, Soft Zr-doped TiO_2 Nanofibrous Membranes with Enhanced Photocatalytic Activity for Water Purification, Sci. Rep. 7 (2017) 1636. doi:10.1038/s41598-017-01969-w.

[90] A. Amorisco, I. Losito, F. Palmisano, P.G. Zambonin, Photocatalytic degradation of the herbicide isoproturon: Characterisation of by-products by liquid chromatography with electrospray ionisation tandem mass spectrometry, Rapid Commun. Mass Spectrom. 19 (2005) 1507–1516. doi:10.1002/rcm.1950.

[91] L. Li, J. Yan, T. Wang, Z.-J. Zhao, J. Zhang, J. Gong, N. Guan, Sub-10 nm rutile titanium dioxide nanoparticles for efficient visible-light-driven photocatalytic hydrogen production, Nat. Commun. 6 (2015) 5881. https://doi.org/10.1038/ncomms6881.

[92] H. Barndõk, D. Hermosilla, C. Han, D.D. Dionysiou, C. Negro, Á. Blanco, Degradation of 1,4-dioxane from industrial wastewater by solar photocatalysis using immobilized NF-TiO_2 composite with monodisperse TiO_2 nanoparticles, Appl. Catal. B, Environ. 180 (2016) 44–52. doi:10.1016/j.apcatb.2015.06.015.